SIZE EXCLUSION CHROMATOGRAPHY OF AGED AND CRUMB RUBBER MODIFIED ASPHALTS

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Keywords: SEC of asphalts, SEC of aged asphalts, SEC of crumb rubber modified asphalts

INTRODUCTION

Preparative size exclusion chromatography (SEC) has been used for several years in our laboratory to provide samples for further analysis and for use in other testing procedures (1). Asphalts have been separated into a first fraction (F-I) that contains nonfluorescing (at 350 nm) materials, and the rest of the asphalt, which is collected in one or more fractions (F-II or F-IIa, F-IIb, etc). The nonfluorescing materials have been shown (1) to contain strongly associating molecules, while the fluorescing materials consist of weakly associating individual and smaller molecules. The fractionation data from these analyses have been related to the rheological property tan delta, and thereby, to rutting and premature pavement cracking. We have developed a high performance liquid chromatography (HPLC) technique that yields these analytical data more rapidly and efficiently than preparative SEC and yet gives chromatograms similar to those derived from preparative SEC. The HPLC procedure described here uses toluene as the carrier as does the preparative procedure.

SEC is a chromatography technique in which separation depends specifically on molecular size and where molecular polarity is a factor only if it promotes molecular association or if the material is of a type to bind to the chromatographic substrate. The column packing has pores of varying sizes that molecules can or cannot enter depending on their size. As a result, the largest molecules, which cannot enter the pores, emerge first from the column(s) and the smallest molecules in the sample, which do enter the pores of the packing and are, therefore, slowed in their passage through the column, emerge last. Some polar molecules may form associated species of varying strengths and if these associations persist under the column conditions they will behave as though they were true molecules with a size similar to the associated species.

A number of other workers have used HPLC/SEC, also known as HPLC-GPC (gel permeation chromatography), to analyze asphalts, among them Jennings et al. (2), who attempted to quantify the data they obtained using a UV/visible diode array detector (DAD). They used tetrahydrofuran (THF) as the carrier and also related their results to highway performance. They also grouped asphalts into four groups according to the asphalts' MSD (molecular size distribution) profiles. Glover et al. (3), used both THF and toluene in their investigations of the HPLC/SEC of asphalts. Brûlé and coworkers published several papers (4) on the HPLC/SEC of unaged and aged asphalts. Bishara et al. (5) have related molecular size data, obtained using an HPLC with a gravimetric finish, to PVN (penetration-viscosity-number), viscosity at 135° C, and other physical properties. Garrick (6) developed a mathematical model from GPC data that predicts GPC profiles from physical properties of asphalts and suggests that the a strong relationship exists between GPC profiles and these physical properties, especially rheological properties. Different combinations of columns with different sized pores have been used in the various investigations.

EXPERIMENTAL

The HPLC equipment consists of a Hewlett Packard Series II 1090 liquid chromatograph with its associated computer hardware and software. There are a DAD, a differential refractive index detector (DRID), a fluorescence detector (FLD), and a fraction collector in place with the HPLC. However, because the sample concentrations used in this work are so large (the DAD, except at high wavelengths, and the FD are swamped), only data from the DRID and gravimetric data are reported here. Fractions are collected using the fraction collector, divested of solvent, and weighed on a balance to provide quantitative data not available from the other detectors.

The column combination in use consists of 2 - 500 Å and 1 - 100 Å 7.8 by 300 mm columns in series. The columns are packed with Phenomenex Phenogel with a 5μ particle size. Toluene is used as the carrier at a flow rate of 1.00 mL/min and the columns are maintained at 40° C. Sample size is around 24 mg of asphalt dissolved in about 220 μL of toluene. The sample is eluted in an hour. However, there is some tailing, so three hours are allowed between sample injections.

Because the samples are quite concentrated, back pressure, probably caused by adsorption of asphalt components in the frits at the ends of the columns, tends to build up after about 75 to 100 runs.

Cleaning is accomplished by backflushing the columns with 25 mL of a 3% methanol in toluene solution at 80° C followed by about 400 mL of toluene. Several samples of an asphalt then are run using normal conditions to condition the columns.

The column combination was calibrated by determination of retention times of several polystyrene standards with known peak molecular weights. Several other compounds of known molecular weight were also examined.

Samples of both unaged, at different concentrations, and asphalts aged to three levels (100°C (212°F) for 12, 20, or 36 hours at 2.07 MPa (300 psi)) were analyzed. Aging was accomplished using the thin film oven/pressure aging vessel technique described earlier (7). Samples of Strategic Highway Research Program (SHRP) asphalts AAB-1 and AAF-1 containing an AC 2.5 Amoco/Wilmington asphalt as a recycling agent were weighed out and then dissolved in toluene. Crumb rubber/asphalt mixtures were prepared by heating a weighed amount of asphalt (SHRP asphalts AAB-1, AAM-1, AAK-2, ABD-1, and ABL-3 were used) at 200°C (392°F) until liquid and then adding a weighed amount of crumb rubber followed by thorough mixing. The crumb rubbers used are both prepared from used tires and include one containing natural rubber designated NR (80 mesh) and one containing both natural and synthetic rubbers designated CR#4 (40 mesh). A sample was then taken which was labeled the zero hour sample. The rest of the CRM was heated under argon at 200°C (392°F) with samples removed at the desired time intervals. As a control, a sample of neat asphalt was heated and sampled under the same conditions as the CRM's. The CRM samples were then treated with toluene in about a 10:1 ratio of toluene to mixture. The partially dissolved samples then were centrifuged for an hour followed by filtration through a 0.22 μ filter using vacuum. The materials left in the centrifuge tube were rinsed further with toluene, centrifuged again, and filtered through the same filter as previously. The rinsing step was repeated and the combined filtrates were divested of solvent, weighed, and the requisite amount of solvent added to give the desired concentration. For all of the asphalts except AAM-1, strings of rubber were seen in the zero and one hour at 156°C (223°F) samples, rubber and carbon black were seen in the samples heated for 24 and 48 hrs, and samples that were heated for longer times seemed not to contain any rubber particles but an increased amount of finely divided carbon black was apparent. For asphalt AAM-1, carbon black first appeared in the 24 hour sample, for the NR mixtures, and increased through the 192 hour sample, while for the CR#4 mixtures, carbon black did not begin to appear until the 168 hour sample and a larger amount was seen in the 192 hour sample.

RESULTS AND DISCUSSION

A calibration curve for the column combination used is shown in Figure 1. The curve shows that the main area of separation for this system lies in the molecular weight range of around 1200 to 14000 Daltons. This is the range seen for SEC fractions F-I through F-IIb for the SHRP core asphalts as reported previously (1).

Early in this work it was necessary to determine the effect of sample size on the chromatogram. Figure 2 shows the results of this study in which it was found that a quite concentrated sample solution was necessary to achieve the desired result, i.e., emulate preparative SEC results. Apparently molecular associations were broken up in the more dilute solutions of asphalt in toluene that occurred when smaller samples were run.

It was necessary to demonstrate the effectiveness of the technique on unaged and aged asphalts so the SHRP core asphalts, both unaged and aged, were all analyzed. Examples of chromatograms of the unaged asphalts AAD-1 and AAF-1 both from the preparative SEC procedure and the HPLC/SEC procedure are shown in Figures 3 and 4 respectively. These figures show the similarity of the chromatograms produced for asphalts for both methods for two quite different asphalts.

Figure 5 shows the overlaid chromatograms of asphalt AAF-1 unaged and aged to three levels as an example of the results for aged asphalts from the technique described here. The chromatograms are drawn so that the largest peak for all four chromatograms is at the same level so that the change in the first part of the chromatogram is readily apparent. The amount of nonfluorescing associating material increases with increased aging. This is in agreement with earlier reports (1, 2, 5).

It was thought desirable to see if this technique could easily differentiate between an untreated asphalt and an asphalt treated with a recycling agent such as a lower viscosity asphalt. Figure 6 shows the overlaid chromatograms of the recycling agent and unaged asphalt AAF-1. As is evident, the recycling agent has as wide an MSD as does the higher viscosity asphalt. The major difference is in the highest molecular size material where the lower viscosity asphalt predominates. Therefore, addition of the recycling agent to the higher viscosity asphalt should show a difference in that region of the chromatogram. However, in Figure 7, where mixtures (5, 10, 25, and 50% AC 2.5) of the recycling agent and AAF-1 are shown, no difference is apparent until the mixture reaches 25% recycling agent. Differences at the 50% level are easily seen in the figure.

Figure 8 shows data from the mixtures of the two grades of asphalt described above for the first five of nine SEC fractions. These curves show that SEC F-I does indeed grow with the addition of increasing concentrations of recycling agent while fractions F-IIa and F-IIb decrease somewhat but, again, the differences are only apparent at concentrations of 25% and above.. This suggests that this particular column combination would not be useful to analyze mixtures of recycling agents with broad MSD's, such as low viscosity asphalts, and another asphalt except at high concentrations. It appears that only recycling agents that have a narrow MSD might be usefully analyzed by this system.

Mixtures of asphalts modified by addition of various crumb rubbers (CRM's) are being studied extensively in our laboratory and it was suggested that HPLC/SEC might be appropriate to determine the fate of the rubber in the CRM's, i.e., where in the MSD does the dissolved rubber appear? Figures 9 through 12 show chromatograms from the study of the separation of mixtures of crumb rubber (CRM's) and asphalt ABD-1. For example, Figure 9 shows overlaid chromatograms for the neat asphalt and the two CRM's before they had been heated except that necessary for mixing. It can be seen that the chromatogram of the mixture containing NR shows a small increase in the chromatogram in the area of large molecular size indicating that some high molecular size material had been incorporated into the asphalt. The other two chromatograms are essentially the same showing no addition of soluble CR#4 to the asphalt prior to further heating. This suggests that the difference in the crumb rubbers is demonstrated very early in the heating regimen, i.e., that NR is solubilized more easily with asphalt ABD-1 than CR#4. Figure 10 shows the effect of heating on the chromatograms of the neat ABD-1. A very small change in the area of large molecular size is seen for the neat ABD-1 on heating from 0 to 96 to 192 hours. Figure 11 shows chromatograms for the mixture of ABD-1 and NR. As can be seen, changes occur in the large molecular size region of the chromatograms. Heating this mixture for as little as an hour has made a significant change in the very large molecular size region of the chromatogram, that is, a peak is seen at the front edge of the chromatogram. Further heating of the sample gradually fills in the area between that peak and the rest of the chromatogram.. This suggests that the rubber particles break down to a initially yield relatively large molecular size material followed by further breakdown to smaller molecular size material. Figure 12 shows chromatograms for the mixture of ABD-1 and CR#4. In this case, the 0 and 1 hour chromatograms are virtually identical, while the leading edge peak of the 24 hour chromatogram and those for higher levels of oxidation show that CR#4 does not begin to break down as early in the heating regimen with ABD-1 as does NR.

Figures 13 and 14 show chromatograms for both neat asphalt AAB-1 and a mixture of AAB-1 and NR respectively. Figure 13 shows chromatograms how the neat asphalt reacted to different periods of heating at 200°C (392°F). Interestingly, the amount of large molecular size materials formed on heating AAB-1 for 48 hours gradually diminished on further heating suggesting these materials broke down to lower molecular weight materials on sustained heating or became materials that are incapable of forming intermolecular associations. Of the asphalts studied so far, this result is peculiar only to AAB-1 and may be a result of the aging occurring in an argon atmosphere. The chromatograms in Figure 14 show that heating the AAB-1/NR mixture leads to an increase in large molecular size materials with increased heating time. Chromatograms are shown for a heating period of up to only 48 hours because further heating showed no further changes in the chromatograms. This lack of further change suggests that further breakdown of the rubber did not occur after 48 hours of heating with asphalt AAB-1 at 200°C (392°F). Similar chromatograms are obtained for the AAB-1/CR#4 mixture.

Chromatograms similar to those shown for asphalt AAB-1 could be shown for neat SHRP asphalts AAK-2 and ABL-3. Asphalt ABL-3 was supposed to be a replacement for SHRP asphalt AAK-2 but SEC chromatograms show significant differences. At any rate, the chromatograms for both the neat asphalts and the CRM's show a steady increase in the large molecular size region with increased heating time with the mixtures showing the larger increase.

Figures 15 and 16 show chromatograms for asphalt AAM-1 and asphalt AAM-1 with NR respectively. Figure 15 shows the chromatograms for the neat asphalt as a function of heating time and demonstrate that heating neat AAM-1 for 72 hours at 200°C (392°F) causes little change but, additional heating to a total of 96 hours caused a significant increase in the area of large molecular size material. On the other hand, heating the AAM-1/NR mixture showed small but significant changes in the large molecular size region through 24 hours of heating at 200°C (392°F) and, after 48 total hours of heating, a very large change. The chromatograms for the neat asphalt after 96 hours of heating and for the asphalt with NR after 48 hours of heating are similar, but very different from those for the other asphalts. This suggests that the source for the for the additional large molecular size material is the asphalt, not the rubber, and that large molecular size materials from the rubber seen in the chromatograms from the other asphalts are "buried" under the curve for the materials from the asphalt. However, because the material appears at a shorter heating time for the CRM than for the neat asphalt, it seems possible that something in the rubber catalyzes the formation of large molecular size materials from the asphalt. This could possibly be explained by the presence of finely divided carbon black in the rubber that begins to make its appearance as the rubber breaks down. Perhaps the carbon black particles supply a focal point for potential SEC F-I materials to associate as dust particles do in crystallization. These associations must be stable in toluene in order to be detected by the DRID.

CONCLUSIONS

The HPLC/SEC technique described, i.e., the column combination, column temperature, solvent, and flow rate, has demonstrated the ability to emulate preparative SEC for unaged asphalts and also give chromatograms for aged asphalts that show an increase of large molecular size material is produced on aging in the TFO/PAV. Calibration of the column combination with materials of known molecular weight shows the major separation occurs in the large molecular size material area of the MSD. In addition, analysis of the CRM's has shown that the breakdown products from the heating of the rubbers of the CRM's at 200°C (392°F) appear in the large molecular size region of the MSD. The response of the two crumb rubbers to heating with the asphalts varies in that NR seems to solubilize sooner than does CR#4 for the same asphalt In addition, the two crumb rubbers respond differently to being heated with different asphalts, i.e., solubilizing more rapidly in one asphalt than in another. This HPLC/SEC system has easily shown these differences.

REFERENCES

1. J.F. Branthaver, J.C. Petersen, R.E. Robertson, J.J. Duvall, S.S. Kim, P.M. Harnsberger, T. Mill, E K. Ensley, F.A. Barbour, and J.F. Schabron, "Binder Characterization and Development. Volume 2: Chemistry. SHRP-A-368. Strategic Highway Research Program, National Research Council, Washington, DC, 39-76 (1993).

2. P.W. Jennings, J.A. Pribanic, M.F. Raub, J.A. Smith, and T.M. Mendes, "Advanced High Performance Gel Permeation Chromatography Methodology", SHRP AIIR-14 Final Report (1991).

3. G.R. Donaldson, M.W. Hlavinka, J.A. Bullin, C.J. Glover, and R.R. Davison, J. Liquid Chrom., 11, 749 (1988).

4. B. Brûlé, G. Raymond, and C. Such, "Relationships among Composition, Structure, and Properties of Road Asphalts", in "Asphaltenes and Asphalts, 1. Developments in Petroleum Science, 40" (T.F. Yen and G.V. Chilingarian, Ed.), Elsevier Science B.V. (1994).

5. S.W. Bishara, R.L. McReynolds, and E.R. Lewis, "Interrelationships between Performance-Related Properties of Asphalt Cement and Their Correlation with Molecular Size Distribution", Transport. Res. Rec., 1323 (1991)

6. N.W. Garrick, J. Mat. Civ. Eng., 6, 376 (1994).

7. AASHTO Designation PP1, Edition 1A, September 1993, "Standard Practice for Accelerated Aging of Asphalt Binder Using a Pressurized Aging Vessel (PAV).

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ACKNOWLEDGEMENTS

The author thanks the Federal Highway Administration for financial support under Contract No. DTFH61-92C-00170. The author also thanks J.C. Petersen, coworkers J.F. Branthaver and R.E. Robertson for encouragement and helpful suggestions in the preparation of this report, J. Greaser for help in preparation of the manuscript, and Anthony Munari for help in preparation of the figures.

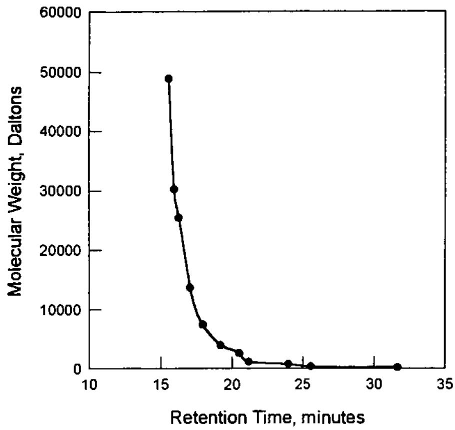

Figure 1. Calibration for column configuration of 2-500 Å and 1-100 Å Phenogel (5μ) columns in series at 40°C (104°F) with 1.0 mL/min toluene carrier

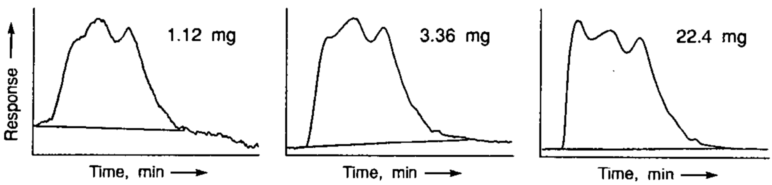

Figure 2. HPLC/SEC chromatograms of asphalt AAD-1 at three sample sizes

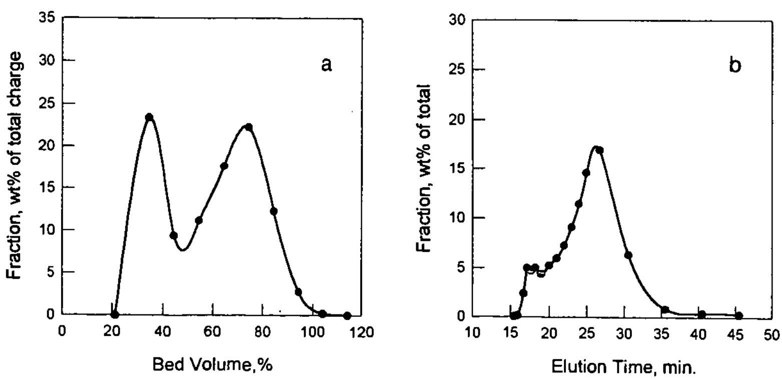

Figure 3. Chromatograms for asphalt AAD-1 from (a) preparative SEC and (b) HPLC/SEC

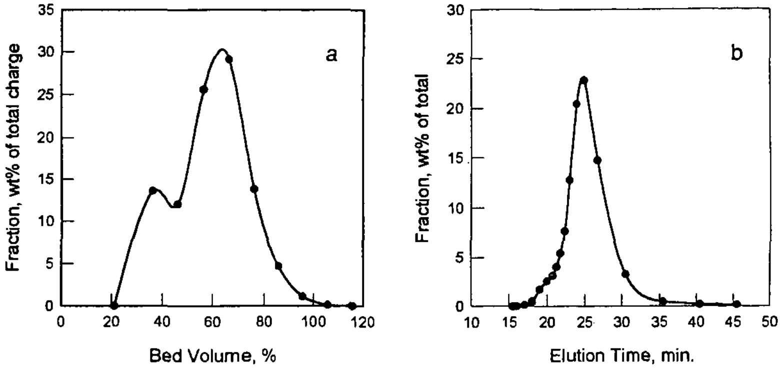

Figure 4. Chromatograms for asphalt AAC-1 from (a) preparative SEC and (b) HPLC/SEC

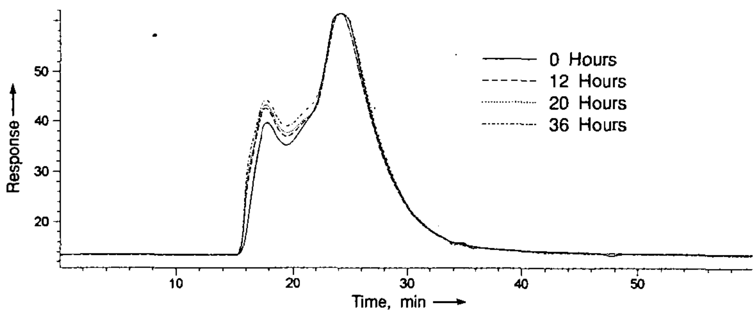

Figure 5. HPLC/SEC chromatograms for asphalt AAC-1 TFO/PAV aged at 100° C (212°F) for different times

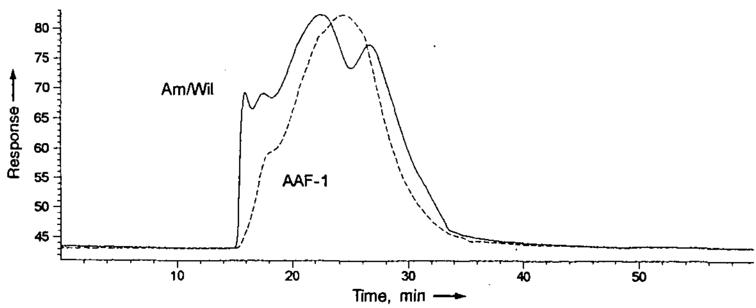

Figure 6. HPLC/SEC chromatograms for asphalt AAF-1 and Amoco/Wilmington AC 2.5

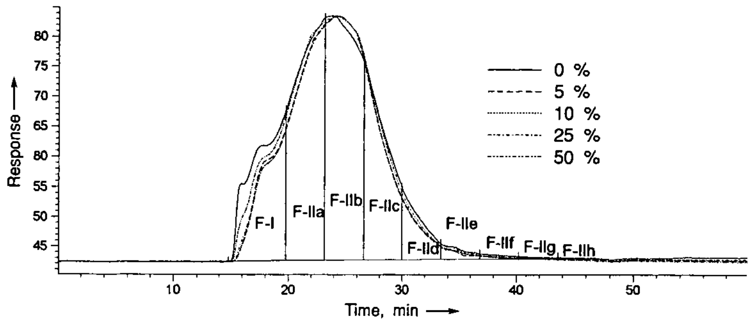

Figure 7. HPLC/SEC chromatograms for asphalt AAF-1 and various percentages of Amoco/Wilmington AC 2.5, showing fraction cutpoints

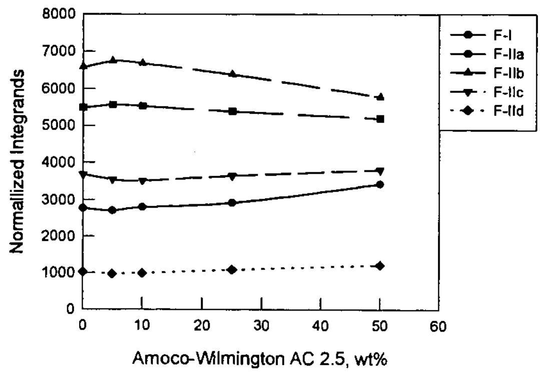

Figure 8. Normalized integrands versus wt% Amoco/Wilmington AC 2.5 in asphalt AAF-1 for various HPLC/SEC fractions

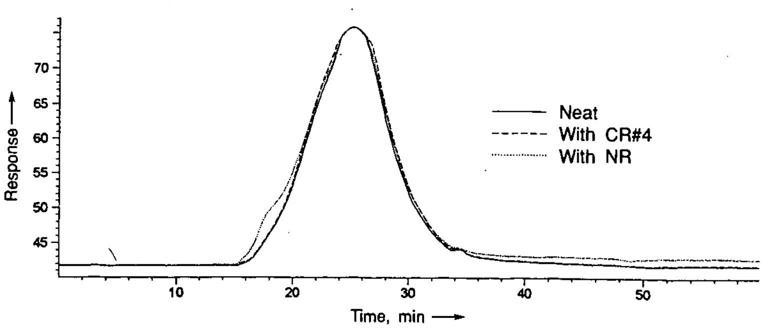

Figure 9. HPLC/SEC chromatograms for asphalt ABD-1 neat and with 12% crumb rubber NR or CR#4 mixed but with no additional heating

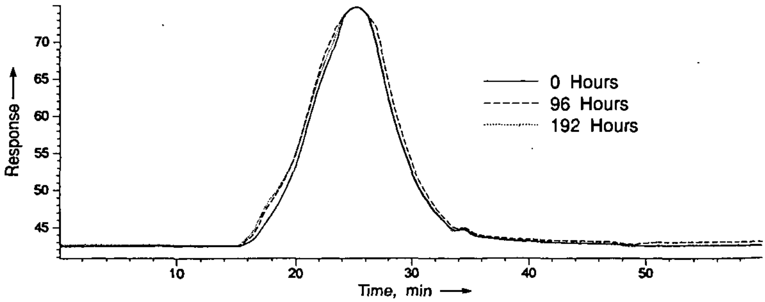

Figure 10. HPLC/SEC chromatograms for neat asphalt ABD-1 heated at 200°C (392°F) for various times

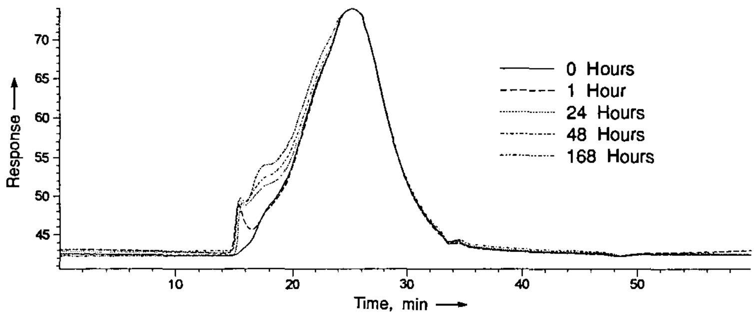

Figure 11. HPLC/SEC chromatograms for asphalt ABD-1 with 12% crumb rubber NR, heated at 200°C (392°F) for various times

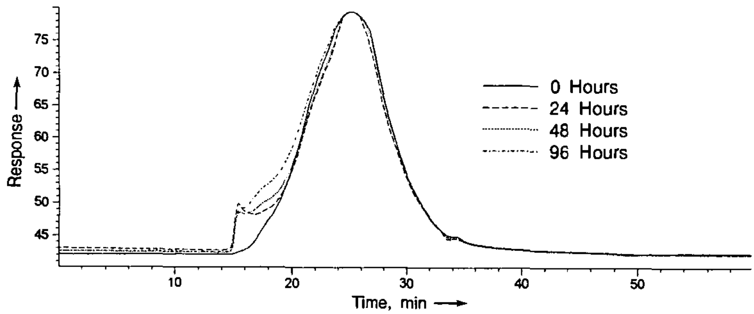

Figure 12. HPLC/SEC chromatograms for asphalt ABD-1 with 12% crumb rubber CR#4, heated at 200°C (392°F) for various times

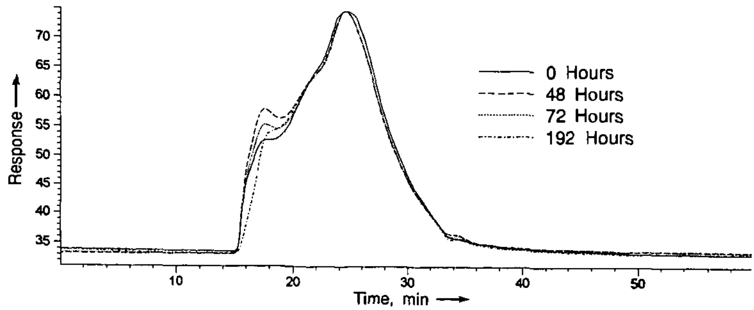

Figure 13. HPLC/SEC chromatograms for neat asphalt AAB-1 heated at 200°C (392°F) for various times

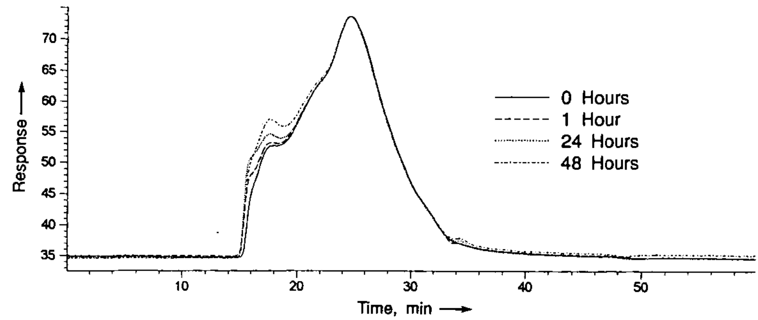

Figure 14. HPLC/SEC chromatograms for asphalt AAB-1 with 12% crumb rubber NR, heated at 200°C (392°F) for various times

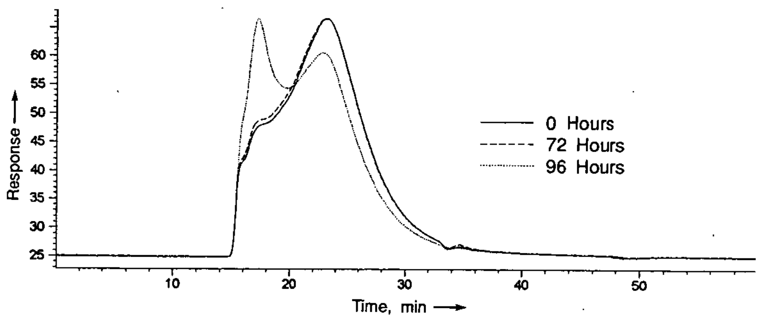

Figure 15. HPLC/SEC chromatograms for neat asphalt AAM-1 heated at 200°C (392°F) for various times

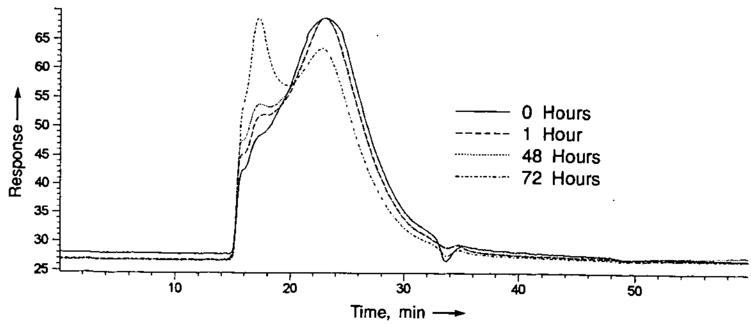

Figure 16. HPLC/SEC chromatograms for asphalt AAM-1 with 12% crumb rubber NR, heated at 200°C (392°F) for various times